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INFLUENCE OF COPPER AND IRON SALTS ON THE BEHAVIOR OF LEATHER IN THE OXYGEN BOMB

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ABSTRACT

Samples of chestnut and quebracho leathers containing from 0.01 to 0.78 percent of copper or iron, were aged in an atmosphere of oxygen at 100 lb/in.² for 7 days at 100° C. The amounts of the nitrogenous materials extractable after this treatment were used as a measure of deterioration. All leathers containing added copper showed more deterioration than the corresponding untreated leathers. In the case of iron, no appreciable increase in the rate of deterioration occurred for values above pH 3.5, and below this value the deterioration appears to be a function of pH rather than of iron content. For equal amounts of metal, that added as the sulfate is more active in accelerating the deterioration of the leathers than that added in the form of the acetate or the lactate.

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I. INTRODUCTION

The deterioration of leather is accelerated by the presence of either copper or iron under certain conditions. Most vegetable-tanned leathers become contaminated with copper and iron during the tanning process. The source of these impurities is the tanning materials which come in contact with these metals, in the grinders and evaporators in which they are prepared. The acidic character of finished leathers causes a further contamination if contact is made in service with surfaces containing these metals. Leathers used for belting and hydraulic packings are most likely to become contaminated by these metals.

The influence of copper and iron on the oxidation of leather and leather-making materials has been studied by a number of investigators. E. W. Merry [1]¹ showed that the addition of copper as copper acetate greatly increased the rate of absorption of oxygen by a solution of American chestnut extract, and that the addition of iron as ferric alum also had an accelerating effect on the absorption of oxygen but

¹ Numbers in brackets indicate references at the end of the paper.

not so great as in the case of copper. R. Faraday Innes [2] studied the effect of iron and copper on leather by accelerated aging with hydrogen peroxide. After experimenting with ferrous sulfate and a copper salt, he concluded that oxidation of either pyrogallol- or catechol-tanned leather is accelerated greatly by iron and to a lesser extent by copper. M. Bergmann [3] and coworkers showed that vegetable-tanned leather was equally damaged by either ferrous sulfate or sulfuric acid solutions having pH values approximately 3.5, which indicated that in this case the effect was not oxidation by the iron but hydrolysis by the acid. J. Jablonski [4] commenting on Bergmann's work believed that deterioration was not observed because air was not freely accessible to the samples. The lack of agreement in the conclusions of these investigators seems to be caused by differences in the conditions under which their experiments were made. This has made desirable a further study of the action of copper and iron salts on leather so that data obtained in the treatment of leathers in the oxygen bomb may be more accurately related to their behavior during normal aging. This investigation consists in a study of the effects produced when leather is impregnated with varying amounts of different salts of these metals and exposed to oxygen in a bomb.

II. MATERIALS AND METHODS

Quebracho- and chestnut-tanned leathers prepared in the experimental tannery at the National Bureau of Standards were used in this investigation. Samples of these leathers were impregnated with varying amounts of copper and iron by soaking in solutions of copper sulfate, copper acetate, ferrous sulfate and ferrous lactate of different concentrations. Ferrous salts were used because they are less readily hydrolyzed at low pH values than the corresponding ferric salts, and for this reason penetrate the leather more readily. The total amounts of these metals in the leathers (see table 1), based on the oven-dry weights of the samples, ranged from 0.01 to 0.78 percent. Although neither copper nor iron is actually present in the leather in metallic form, for convenience, reference is usually made to the quantity in terms of the metal.

The amounts of copper in the leathers were determined [6] as follows: The ash from a 10-g sample was leached with a mixture of sulfuric and nitric acids. After diluting, filtering, and acidifying further with nitric acid the solution was subjected to electrolysis. This treatment deposited most of the copper, which was weighed. The last traces of copper were determined by passing hydrogen sulfide into the electrolyzed solution, filtering and igniting the precipitate and weighing as copper oxide.

In determining the iron [7], the ash was treated in the same way as in the determination of copper. The nitric acid was then removed by heating the solution until white fumes of sulfuric acid were evolved. The solution was diluted and acidified further with concentrated sulfuric acid. The iron was reduced with metallic zinc and then determined by titrating with 0.1 *N* potassium permanganate solution.

In making the tests in the oxygen bomb, pieces of the leathers, approximately 1½ by 3 in., were dried in an oven at 100° C for 24 hours. At the end of this time, they were placed in the bomb in an atmosphere of oxygen at 100 lb/in.² and 100° C, and aged under these conditions for 7 days. The extent of the deterioration was deter-

mined by the percentage of the total amount of the nitrogenous materials extracted from the aged samples by water and 0.1 *N* sodium carbonate solution. The method used in extracting this nitrogenous material and a description of the oxygen bomb used are given in a previous report [5].

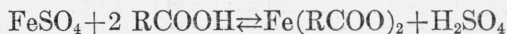
III. RESULTS AND DISCUSSION

1. pH CHANGES

In a previous investigation [8] at the National Bureau of Standards on the effects of sulfuric acid on leather, it was found that those leathers, containing sulfuric acid, whose water extracts had pH values below 3, deteriorated most rapidly under normal aging conditions. A study of the behavior of leather in the oxygen bomb [5] also indicated that deterioration occurred most rapidly below pH 3. For these reasons, it is important to consider the pH factor in a study of the effect of copper and iron salts on the deterioration of leather, in order to distinguish between deterioration caused by the hydrolytic action of acids and that caused by the presence of the metals.

When a salt formed by a strong acid and a weak base, such as copper or ferrous sulfate, is dissolved in water, the solution shows an acid reaction. The degree of acidity under these conditions obviously depends in part upon the strength of the acid from which the salt is formed. Solutions of copper acetate and ferrous lactate therefore have higher pH values than those of the sulfates, and when added to leather may be expected to cause a smaller increase in acidity.

The pH values of the various concentrations of salt solutions in which the leathers were soaked, as well as those of the treated leathers before and after exposure in the oxygen bomb, are given in table 1. The initial pH values of the treated leathers are in most cases lower than either that of the solution or that of the original leather, which indicates that a chemical change has taken place between the leather and the salt. This change is probably brought about by the salt reacting with the tannic acid to form an insoluble tannate as shown for ferrous sulfate by the equation, where RCOOH represents the tannic acid.



The formation of the insoluble tannate causes this reaction to proceed to the right and form sulfuric acid. The same reaction takes place with the acetates and the lactates, but since these salts form weak acids the pH values are not lowered to the point where deterioration is caused by acidity. This indicates that the influence of acidity has, to a large extent, been eliminated for those leathers treated with copper acetate and ferrous lactate, since none of these samples had pH values below 3.

During exposure in the bomb, the acidity of the leather tends to increase, as shown by a decrease in its pH value. This indicates that weak organic acids are formed by oxidation of the tannins. The magnitude of the pH change depends upon the initial pH and the salt used in impregnating the leather. Leathers with initial pH values above 4 show rather large changes during exposure. At pH values below 4, leathers treated with the sulfates show the largest changes (see table 1). The pH values of the leathers treated with the higher

amounts of the sulfates dropped below 3 during exposure in the bomb. In all cases the pH values of the leathers treated with the lactates and the acetates remained above 3 during exposure.

TABLE 1.—*Data on the effect of copper and iron salts on leather*

Treatment	Treating solution		Quebracho leather				Chestnut leather				
	Concentration	pH	Metal present dry basis	pH changes		Total nitrogen dissolved	Metal present dry basis	pH changes		Total nitrogen dissolved	
				Initial	After exposure in bomb			Initial	After exposure in bomb		
Untreated (copper determined)	Percent		Percent	0.015	5.20	3.74	Percent	0.04	3.83	3.32	Percent
Copper sulfate	0.19	4.84	.042	4.66	3.56	8.9	.07	3.78	3.44	36.1	
Do	.38	4.60	.07	4.54	3.57	11.2	.11	3.61	3.39	37.6	
Do	.76		.15	4.27	3.34	24.1	.20	3.49	3.14	46.9	
Do	1.52		.31	4.05	3.17	35.8	.33	3.25	3.00	47.6	
Do	3.93	3.70	.71	3.71	2.85	64.7	.58	3.09	2.95	68.0	
Copper acetate	.16	5.84	.067	5.18	3.62	8.2	.086	3.79	3.27	35.5	
Do	.32	5.74	.099	4.79	3.55	11.3	.10	3.84	3.30	40.3	
Do	.64	5.60	.19	4.62	3.52	15.8	.22	3.78	3.24	40.7	
Do	1.28	5.50	.29	4.45	3.52	17.8	.39	3.76	3.27	41.0	
Do	3.20	5.30	.52	4.44	3.54	30.9	.65	3.74	3.28	43.8	
Untreated (iron determined)											
Do			.009	5.00	3.94	3.1	.020	3.79	3.46	24.0	
			.012	5.06	3.98	1.8	.023	3.84	3.42	26.4	
Ferrous sulfate	.55	3.97	.047	4.40	3.68	3.3	.065	3.62	3.20	40.5	
Do	1.11	3.60	.12	3.92	3.47	4.8	.13	3.20	2.96	59.5	
Do	2.22	3.59	.21	3.52	3.18	5.7	.19	2.95	2.78	66.3	
Do	4.44	3.35	.36	3.34	2.92	11.2	.38	2.70	2.62	88.0	
Do	8.88	3.07	.73	3.04	2.63	34.6					
Do	5.94	3.42	.71	3.24	2.86	13.4					
Do	7.44	3.30	.78	3.15	2.76	20.9					
Ferrous lactate	.55	5.16	.082	4.44	3.82	2.1	.115	3.64	3.38	25.4	
Do	1.11	5.14	.15	4.14	3.71	2.5	.15	3.49	3.32	29.5	
Do	2.22	5.10	.21	3.82	3.66	3.3	.26	3.38	3.26	33.6	
Do	4.44	4.98	.31	3.60	3.54	4.8	.47	3.22	3.16	45.2	
Do	8.88	4.76	.42	3.54	3.50	5.4	.49	3.20	3.20	43.6	
Do	14.28	4.42	.65	3.54	3.50	6.6					
Sulfuric acid	0			4.98	3.71	3.6		3.74	3.47	26.6	
Do	.17			4.34	3.47	3.6		3.47	3.12	31.5	
Do	.35							3.37	2.95	30.3	
Do	.68			3.74	3.24	5.6		3.20	2.88	33.1	
Do	.85							3.03	2.82	34.6	
Do	1.25			3.25	2.92	6.1		2.78	2.64	45.2	
Do	1.70			2.78	2.70	12.0		2.68	2.52	47.5	
Do	2.50			2.58	2.37	24.6		2.48	2.46	64.3	
Do	3.50			2.30	2.28	38.7					

* These two treatments were made with a different sample of ferrous sulfate.

2. EFFECT OF COPPER SALTS ON THE DETERIORATION OF LEATHER

The effect of copper on the deterioration of chestnut- and quebracho-tanned leathers is shown in figures 1 and 2. In figure 1 the extent of the deterioration of the leathers treated with copper sulfate and copper acetate is shown as a function of the initial pH and is compared with that of similar leathers treated only with sulfuric acid. The percentages of copper in the samples are shown beside the plotted points. This comparison indicates that leather is very sensitive to deterioration in the presence of copper. The action of copper appears to be catalytic, since the deterioration takes place in the presence of comparatively small amounts of the metal. The same conclusions

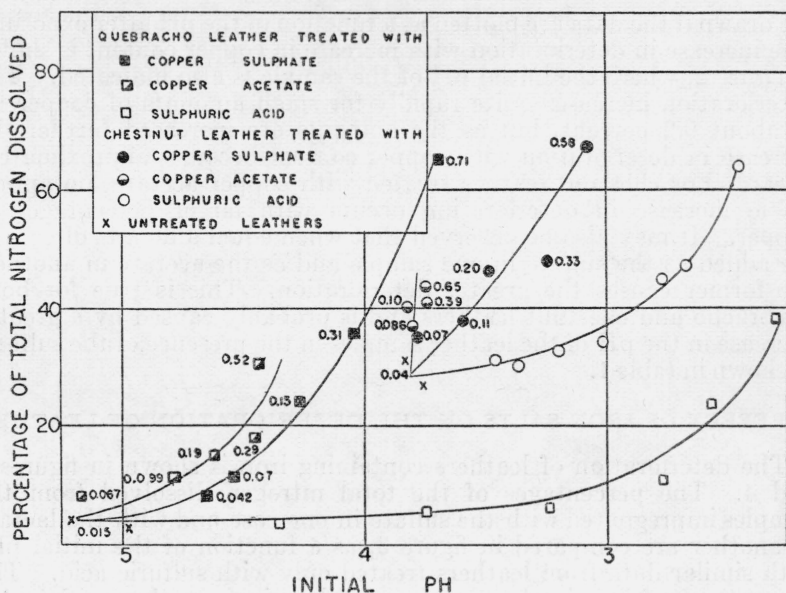


FIGURE 1.—Increase in the amounts of the total nitrogen dissolved as a function of the initial pH values of leathers treated with copper salts, and with sulfuric acid.

Figures beside the plotted points are the percentages of copper present in the samples.

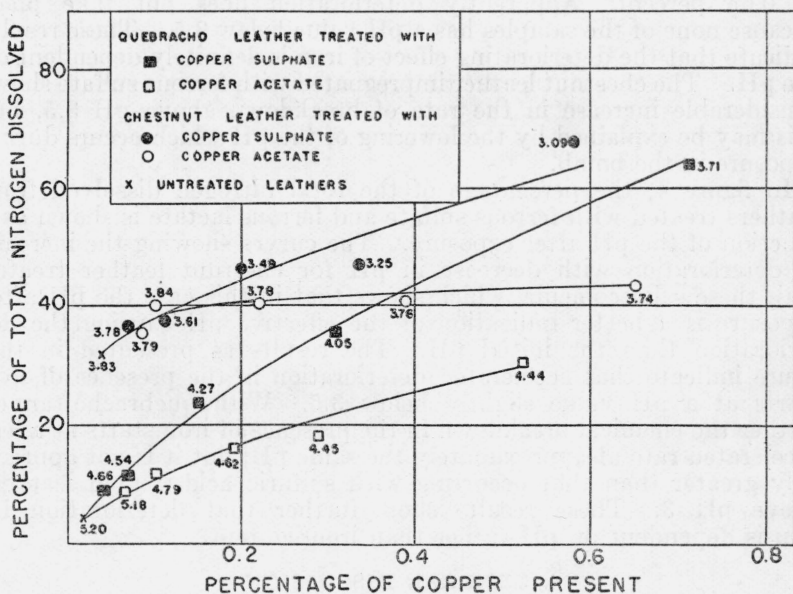


FIGURE 2.—Increase in the percentages of the total nitrogen dissolved with increase in copper content.

Figures beside the plotted points are the initial pH values of the samples.

are drawn if the data are plotted as a function of the pH after exposure. The increase in deterioration with increase in copper content is shown in figure 2, where the initial pH of the sample is also indicated. The deterioration increases quite rapidly for small amounts of copper up to about 0.2 percent, but as the amounts are increased further the increase in deterioration with copper content becomes approximately linear. For chestnut leather treated with copper acetate, no appreciable increase in deterioration occurs with larger percentages of copper. It may also be observed that when equal amounts of copper are added as the sulfate in one sample and as the acetate in another, the former causes the greater deterioration. This is true for both quebracho and chestnut leathers and is probably caused by a greater decrease in the pH of the leather samples in the presence of the sulfate, as shown in table 1.

3. EFFECT OF IRON SALTS ON THE DETERIORATION OF LEATHER

The deterioration of leathers containing iron is shown in figures 3 and 4. The percentages of the total nitrogen dissolved from the samples impregnated with the sulfate in one case and with the lactate in another are compared in figure 3, as a function of the initial pH, with similar data from leathers treated only with sulfuric acid. The percentages of iron in the samples are also given on the graph. According to the data, the deterioration of the quebracho leather treated with ferrous sulfate and that of the chestnut leather containing ferrous lactate, is accelerated by iron at pH 3.5 and below. Quebracho leather treated with ferrous lactate shows no appreciable deterioration even though the amounts of iron present vary from 0.08 to 0.65 percent. Apparently deterioration does not take place because none of the samples has a pH value below 3.5. These results indicate that the deteriorating effect of iron is definitely dependent on the pH. The chestnut leather impregnated with ferrous sulfate shows considerable increase in the rate of breakdown above pH 3.5, but this may be explained by the lowering of the pH which occurs during exposure in the bomb.

In figure 4, the percentage of the total nitrogen dissolved from leathers treated with ferrous sulfate and ferrous lactate is shown as a function of the pH after exposure. The curves showing the increase in deterioration with decrease in pH for chestnut leather treated with these salts coincide, which shows that in this case the pH after exposure is a better indication of the effective pH causing the deterioration than the initial pH. The results as presented in this figure indicate that accelerated deterioration in the presence of iron starts at a pH value slightly below 3.5. With quebracho-tanned leather the chemical breakdown in the presence of iron starts at a less accelerated rate at approximately the same pH, but it is not appreciably greater than that occurring with sulfuric acid-treated leathers above pH 3. These results show further that deterioration by iron is dependent on pH rather than iron content.

4. GENERAL DISCUSSION

The mechanism of the action of copper and iron in accelerating the deterioration of leather appears to be catalytic, since deterioration occurs in the presence of comparatively small amounts of the metals. However, the conditions under which the two metals are effective

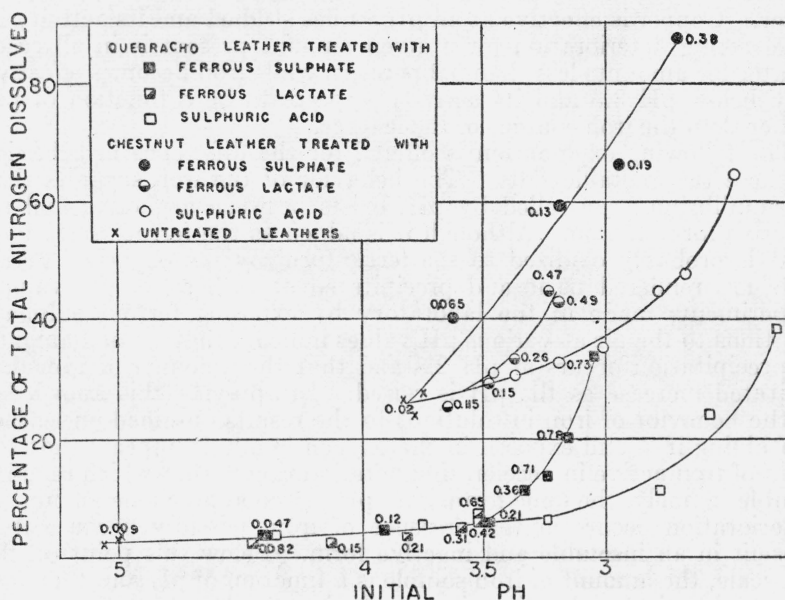


FIGURE 3.—Increase in the amounts of the total nitrogen dissolved as a function of the initial pH values of leathers treated with iron salts and with sulfuric acid.

Figures beside the plotted points are the percentages of iron present in the samples.

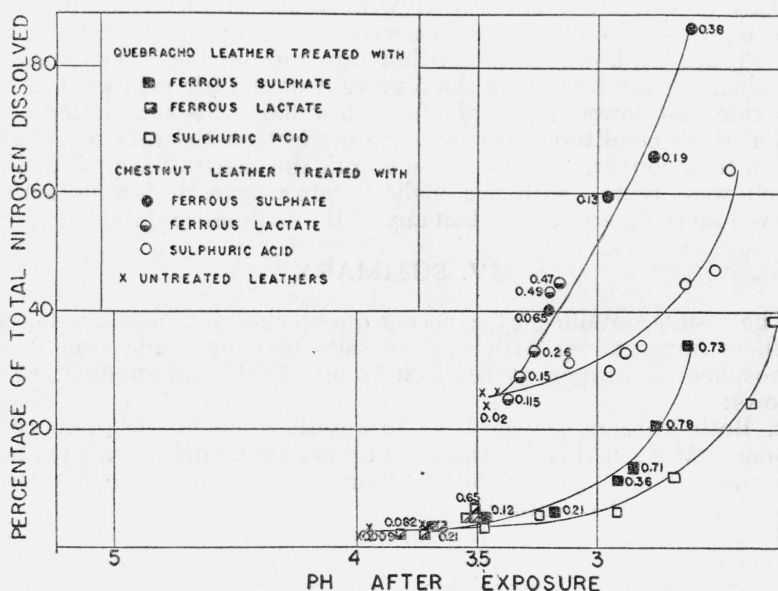


FIGURE 4.—Increase in the amounts of the total nitrogen dissolved as a function of the pH after exposure of leathers treated with iron salts and sulfuric acid.

Figures beside the plotted points are the percentages of iron present in the samples.

differ. Copper is effective at all pH values studied and its activity in accelerating deterioration for a given amount present is in all cases greater for amounts less than 0.2 percent, while iron becomes effective only below pH 3.5 and its activity appears to be a function of pH rather than the iron content of the leather.

The following explanation is offered for the difference in behavior of these two metallic salts. The behavior of the iron suggests that an equilibrium, controlled by pH, exists between an active and an inactive form of iron. Although it is added as the ferrous salt, most of it is probably oxidized to the ferric form by the oxygen. Ferric salts are rendered basic and precipitated at rather low pH values. Experiments made in the laboratory by exposing ferrous sulphate solutions to the air at various pH values indicate that a small amount of precipitation occurs at pH 2.8 and that the amounts of iron precipitated increase as the pH is raised. In applying this knowledge of the behavior of iron in solutions to the results obtained on leather containing iron and exposed in the oxygen bomb, it appears that the form of iron active in accelerating deterioration is that which remains soluble; namely, the ionic form. At pH 3.5 no appreciable amount of deterioration occurs in the presence of iron, possibly because it is present in an insoluble and inactive form. Below this point on the pH scale, the amount of iron soluble is a function of pH and therefore the acceleration of deterioration by the iron is also a function of pH. For equal amounts of metal added, the sulfates accelerate deterioration of chestnut and quebracho leathers at a greater rate than either the acetates or the lactates, apparently because the sulfates cause a greater increase in acidity.

Where experimental conditions are comparable, the results obtained in this investigation agree well with those obtained by previous investigators. Bergmann [3] observed no effect by iron above pH 3.5. Innes [2], however, found that iron had an effect which may be explained on the basis that the 5 percent of sulfuric acid used in the peroxide test lowered the pH far below 3.5. He also stated that under these conditions iron had more effect on the rate of deterioration than copper. In the present work the chestnut-tanned leather which was treated with the highest percentages of ferrous sulfate showed more deterioration than any of the samples containing copper.

IV. SUMMARY

The results obtained by exposing quebracho- and chestnut-tanned leathers impregnated with various salts of copper and iron to an atmosphere of oxygen at 100 lb/in² and 100° C, are summarized as follows:

1. Both leathers are sensitive to deterioration in the presence of copper. Most of this deterioration occurs above pH 3. All leathers containing added copper showed more deterioration than the corresponding untreated leathers.
2. The increase in the rate of the deterioration with increasing copper content is most rapid for amounts less than 0.2 percent.
3. With iron, no appreciable effect on the rate of deterioration occurs above pH 3.5 and at lower pH values the deterioration appears to be a function of pH rather than iron content.

4. For equal amounts of metal, that added as the sulfate is more active in accelerating the deterioration of the leathers than that added in the form of the acetate or the lactate.

5. The action of the copper and iron salts on the leathers appears to be catalytic, since deterioration occurs in the presence of comparatively small amounts of the metals.

V. REFERENCES

- [1] J. Int. Soc. Leather Trades Chem. **16**, 239 (1932).
- [2] J. Int. Soc. Leather Trades Chem. **19**, 109 (1935).
- [3] Collegium 451 (1934).
- [4] Collegium 7 (1935).
- [5] J. Am. Leather Chem. Assn. **32**, 314, 1937; J. Research NBS **18**, 713 (1937) RP1004.
- [6] Harold A. Fales, *Inorganic Quantitative Analysis*, p. 389-390 (The Century Co., New York, N. Y., 1925).
- [7] Edward G. Mahin, *Quantitative Analysis*, p. 218, (McGraw-Hill Book Co. New York, N. Y., 1924).
- [8] J. Am. Leather Chem. Assn. **28**, 125 (1933); BS J. Research **10**, 559 (1933) RP547.

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